Preperation and properties of ultra-high stength polyethylene fibres.

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SUMMARY

This thesis describes a study on the preparation of ultra-strong polyethylene fibres by gel-spinning and hot-drawing, on their morphology, and on their melting behaviour and mechanical properties.

Gel-spinning involves the processing of a semi-dilute solution of ultra-high molecular weight polyethylene (UHMWPE) in paraffin-oil into a continuous gel-filament. After extraction of the gel-filament with n-hexane a porous fibre remains, which can be extensively drawn at elevated temperatures. The resulting highly oriented polyethylene fibres can attain a tensile strength at break of up to 5 GPa and a Young's modulus of up to 160 GPa. On a molecular level a network of long chain molecules, containing relatively few chain entanglements, is stretched out as far as possible and the resulting oriented state is fixed by crystallization. Polyethylene with a very high molecular weight ($\overline{M}_w = 4 \times 10^6$) is used so as to minimize the number of chain ends. This is because chain ends will disturb the crystal lattice in the finally oriented structure and lower the number of covalent bonds, which lowers the strength of the polyethylene fibres.

The main objective of this work was to elaborate on the effect of the main process variables during gel-spinning/hot-drawing on the properties of the UHMWPE fibres. In so doing one should gain a better understanding of the molecular mechanism underlying the fibre formation process. Furthermore it was important to elucidate the fracture mechanism in the filaments in an attempt to clear up the large discrepancy between the theoretical strength in polyethylene of 25 GPa and its practical limit of 5 GPa.

The ultimate strength of the filaments after hot-drawing

was strongly dependent on the speed, with which they had been collected during spinning at a spinning temperature of 170°C (Chapter 2). Fibres produced at a spinning rate of ca. 1.5 m/min, generally had a strength between 3 and 4 GPa after hot-drawing. Increasing of the spinning rate by applying extrudate stretching resulted in a dramatic decrease of the tensile properties after subsequent hot-drawing. This has been attributed to elastic turbulence which affects the flow patterns in the spinning solution and thereby also the morphology in the as-spun fibres. Already at low flow rates, i.e. about 1.5 m/min, the molecular network in the polyethylene solution splits up into long bundle-like flow units, each consisting of bundles of elongated chain parts connected via entanglements to large clusters of unoriented molecules. Subsequent quench crystallization gave rise to a morphology in the as-spun fibres, of large folded-chain lamellae interconnected by several chain-extended fibrils, which could be highly drawn. At larger flow rates the original long flow units in the spinning solution are destroyed, due to the occurrence of elastic flow instabilities, i.e. elastic turbulences, in the solution. As a result the coherence of the entanglement network in the as-spun fibres is lost and such quickly spun fibres show poor drawing properties. The generation of elastic turbulences in the flow-field during spinning at high take-up speeds, could be suppressed by the addition of a small amount of Al-stearate to the spinning solution. This enables fibres to be made with a tensile strength between 2.5 and 3 GPa after spinning at winding speeds up to 300 m/min and subsequent hot-drawing.

Besides the influence on the morphology of the as-spun fibres, the elongational flow field applied to the UHMWPE also had a marked effect on the chain length of the individual molecules (Chapter 3). Due to mechanical degradation in the flowing polymer, the molecular weight of the polyethylene was reduced to a limiting value of 1.5×10^6. Accordingly, the generally accepted rule that the ultimate strength in fully oriented polymers increases with increasing molecular weight seems to be bound to a practical limit.

As was already mentioned, the orientation of the gel-spun UHMWPE fibres was completed in a hot-drawing treatment. In this process the original "shish-kebab" like morphologies in the as-spun fibres were converted into smooth fibrillar structures. A leading parameter in this process, determining the ultimate tensile properties of the filaments, appeared to be the draw ratio. Both the tensile strength at break and the Young's modulus increased almost linearly with draw ratio (Chapter 3). The maximum draw ratio of the filaments, which could be accomplished, steadily increased with drawing temperature. The optimum drawing temperature was 148°C. Filaments produced at a low spinning rate of ca. 1 m/min could readily be drawn to draw ratios of about 100 at this temperature.

The deformation mechanism in the hot-drawing process was also affected by the drawing temperature, as could be concluded from elongational viscosity measurements in the temperature range of 100-150°C (Chapter 4). From the temperature dependence of the elongational viscosity a value for the activation energy of the drawing process was estimated. In the range of 100-133°C separate fibrillar units were sliding past each other, which resulted in an activation energy of 50 kJ/mol. Hot-drawing at temperatures between 133 and 143°C required a higher activation energy of 150 kJ/mol, which was caused by an aggregation of the elementary fibrils. At temperatures above 143°C, the activation energy was strongly dependent on draw ratio and amounted to values in the range between 200-600 kJ/mol. Molecular orientation in this region is accomplished by a slippage of individual molecules past each other, whereby entanglement connections prevent the molecules from recoiling.

A further insight into this high temperature drawing mechanism was obtained from a study of the melting properties of fibres drawn to various draw ratios at 148°C (Chapter 5). This study revealed that the transformation of the original shish-kebab structures into smooth fibrils, initially proceeds by pulling the elastically inactive loops (which form the lamellar overgrowth in the shish-kebabs), taut between entanglements. In subsequent stages of the drawing process the elongated molecules slip through the entanglement couplings. In this

process several entanglements, located near the end of the molecules, are removed, until in the fully drawn fibre a minimum number of 2.5 entanglements per molecule remains. The smooth fibrils in the fully drawn fibre were found to be composed of a continuous structure of the thus elongated molecules. In this structure fully aligned orthorhombic crystallites with a length of ca. 70 nm are interspersed with defect domains of ca. 4 nm in length (which contain the trapped entanglements and the chain ends).

Constrained melting experiments made it possible to study a solid-solid phase transition from the orthorhombic to a hexagonal phase. This transition takes place in the UHMWPE fibres at about 150^{o}C if the molecules cannot randomize upon heating, i.e. when they are fully elongated between entanglements. The heat effect associated with this phase transition in fully crystalline polyethylene was estimated to be 205 kJ/kg. The heat of fusion of the hexagonal phase was found to be 81 kJ/kg.

The fracture mechanism of the fully drawn UHMWPE fibres is largely connected with the presence of a fibrillar structure, containing topological defect regions (Chapter 6). The relatively short lifetimes of the filaments in dead-load tests made it clear that their strength is mainly determined by the lateral bond strength between the molecules. This can also be seen from the low activation energy of the fractures process (60-75 kJ/mol). It was demonstated using electron microscopy that fracture in the fibres is initiated at surface irregularities, such as kink bands. In the neighbourhood of such kink bands a crack is formed which penetrates the interior of the filament by moving alongside the fibrils until it meets a defect region. Here the fibrils are cut through. Since such kink bands occurred more frequently in thicker filaments, the ultimate strength of the fibres was dependent on their diameter. Analogous to early observations of Griffith on glass fibres, the strength of the UHMWPE fibres was found to be inversely proportional to the square root of their diameter. Extrapolation to zero diameter resulted in a value for the strength of a flawless fibre of

26 GPa, which corresponds very closely to the theoretical strength of polyethylene.

Finally, a new, more straightforward method was developed for the preparation of ultra-strong polyethylene fibres by means of suspension-spinning/hot-drawing (Chapter 7). Suspension-spinning comprises the flow of a stabilized suspension of UHMWPE powder through a long heated tube, which acts as the spinning apparatus. This means that the dissolution and the spinning of the polymer, which were two separate steps in the gel-spinning procedure, are now combined into a single step. Preliminary experiments showed that it was possible to produce fibres with a tensile strength at break of 3.8 GPa by this method.